



Investigation of phosphorous doping effects on polymeric carbon dots: Fluorescence, photostability, and environmental impact

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ABSTRACT

Carbon dots have arisen as a potential alternative to traditional quantum dots since they fluoresce but are synthesized from sustainably sourced green chemicals. Herein, fluorescent nitrogen-doped polymeric carbon dots (CDs) were synthesized by using citric acid (CA) or malic acid (MA) as carbon precursors and ethylenediamine as the nitrogen precursor. Additionally, phosphoric acid was used as a doping agent for each type of CDs to evaluate the impact of incorporating phosphorus into the nanoparticles. Thus, four kinds of doped CDs (N-doped or N, P co-doped) were obtained and named as CACDs, CA-P-CDs, MACDs, and MA-P-CDs. Quantum yield and fluorescence lifetime analysis indicate that phosphorus doping of up to *c.a.* 10 wt% does not induce a remarkable influence on CD photoluminescence. The photostability of the N, P co-doped MACDs (MA-P-CDs), however, was observed to increase compared to the N-doped MACDs under 350 nm UV (UV-B) exposure. Lastly, to assess the impact of this emerging nanoparticle on prokaryotes, the bacterial toxicity of these CDs was tested using *Shewanella oneidensis* MR-1 as a model microorganism. Interestingly, the CDs exhibited no toxicity in most cases, and in fact facilitated bacteria growth. Hence, this work suggests that CDs are potentially eco-friendly fluorescent materials.

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1. Introduction

Since the discovery of carbon dots (CDs) during the purification of arc-discharged single-walled carbon nanotubes (SWCNTs) in 2004 [1], they have become a carbon nanoallotrope of great interest [2,3]. Generally, CDs are zero-dimensional (0D) carbon nanoparticles of 2–10 nm diameter with quasi-spherical morphology. The majority of the carbon within the CDs is sp^3 -hybridized and usually exists as amorphous carbon, different from another 0D carbon nanoallotrope, nanodiamonds (NDs), which consist of highly crystalline domains [2–5]. Due to their excellent photoluminescence, stability, low cost, and easy preparation [4,6–8], CDs have been under intense investigation for their potential applications in sensing [9–14], bioimaging or cell labelling [3,15–17], drug

delivery [16,17], white light-emitting devices [7,18], and energy conversion [19–21].

A variety of methods have been developed to generate fluorescent CDs in the past decade. Roughly, these synthesis approaches can be classified as either “top-down” or “bottom-up” [4,22]. Generally, the “top-down” route involves breaking down bulk carbon sources, like graphite [19,23], carbon fibers [24,25], or carbon nanotubes [1,26], into tiny carbon nanoparticles, namely, carbon dots. Available “top-down” synthetic techniques exploit electrochemistry, arc discharge, laser ablation, or plasma treatment [27,28]. Conversely, the “bottom-up” route refers to the construction of amorphous carbon nanostructures from molecular precursors such as saccharides [29], organic acids [8,13], or amino acids [30,31] via combustion methods, hydrothermal/solvothermal treatment, or microwave irradiation [4,27]. To be more specific, microwave heating-based synthesis capitalizes on internal precursor molecular rotation transitions coupling with external electromagnetic irradiation [32]. Thus, the heating efficiency is not

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related to the thermal conductivity of the precursors, realizing an immediate on/off switching in heating [32,33]. Hence, compared to other methods, microwave-assisted thermal treatment conserves both time and energy, and might even avoid undesirable side reactions or facilitate new reaction routes [32–34]. Thus, microwave heating has been broadly used as a promising method to prepare stable and highly photoluminescent CDs [7,8,35–39].

Doping heteroatoms into CDs has been a popular concept for potentially improving the performance of carbon nanomaterials [40–42]. A significant number of doped CD studies have been reported, most of them doped with non metal heteroatoms such as N [43–45], S [44,46], B [47–49], or P [49–51]; there are also rare cases of metal atom dopants such as Cu [52], Mg [53] and Gd [54]. In general, doped CDs have exhibited improved optical properties compared to non-doped CDs such as higher quantum yields and longer fluorescence lifetimes, especially when a functionalization route is used. The chemical identity of the doped heteroatom influences the electron distribution within the CDs, altering the band-gap energy and thus improving the CD photoluminescence [55,56]. Currently, there are a lack of systematic investigations on the effects of doping on the properties of CDs. To address this issue, a series of polymeric CDs with different levels of doping were synthesized herein to compare the fluorescence properties of these polymeric CDs, and to elucidate whether doping is an effective strategy for polymeric CD performance improvement. It is important to mention here that there is a range of names used for carbon dot nanomaterials, including carbon quantum dots, graphene quantum dots, and polymer dots. To avoid confusion, the products made in this work will be identified as polymeric CDs because they are generated by carbonizing polymerized intermediates.

CDs have exhibited comparable quantum yields to traditional semiconductor quantum dots (QDs), and they are free of toxic heavy metal ions [2,4]. Thus, they are assumed to be of low toxicity and may serve as a green alternative to QDs [57–59]. Up to now, most CD research has been heavily focused on their synthesis and applications, while only a few reports have addressed their potential environmental consequences, let alone the comparative impact of modified/doped CDs [60,61]. To evaluate their true potential, it is necessary to characterize CD photoluminescence in parallel with a toxicity assessment relevant to the potential release of CDs into the ecosystem – a specific goal of this study. Microorganisms, located at the bottom of the food web, are ubiquitous [62] and thus likely to first interact with and respond to nanomaterials released into the environment. *Shewanella oneidensis* MR-1 (*S. oneidensis* MR-1), first discovered in Lake Oneida, NY [63], is a species of Gram-negative bacteria important in the ecosystem based on its notable ability to reduce metal oxides via dissimilatory reduction under anaerobic conditions [64]. In addition, *S. oneidensis* MR-1 has been applied in nanomaterial toxicity screening, including studies of silver nanoparticles (Ag NPs) [65], gold nanoparticles (Au NPs) [66], and Li-ion battery materials [67]. Thus, *S. oneidensis* MR-1 has been chosen herein as the model microorganism to evaluate the potential environmental impact of N- and P-doped polymeric CDs.

In this manuscript, we will demonstrate the synthesis, material characterization, photostability tests, and bacterial toxicity of nitrogen and phosphorous-doped polymeric carbon dots. This is the first effort in a larger set of experiments, and future work will further explore the underlying chemical or physical properties of the polymeric carbon dots that result in the exciting photoluminescent properties.

Specifically, this work explores the impact of phosphorous doping on nitrogen-doped polymeric CDs. Based on quantitative analysis, we find that doping phosphorus into the polymeric CD structure using a phosphorous-containing precursor does not

significantly impact polymeric CD fluorescence behavior including quantum yield and lifetime. The phosphorus-doped polymeric CDs, however, do demonstrate enhanced photostability during UV-B exposure (350 nm) compared to undoped polymeric CDs. Interestingly, comparing the photoluminescence performance of nitrogen-doped polymeric CDs generated from citric acid, containing three carboxylic acid groups, versus the two carboxylic acid groups in malic acid, shows significant differences, likely due to their different crosslinking patterns with ethylenediamine. Furthermore, the bacterial toxicity results indicate that phosphorous doping did not increase toxic effects towards the bacteria but potentially stimulated bacteria growth in most cases, highlighting the potential of polymeric CDs as an emerging fluorescent nanomaterial with minimal adverse environmental effects.

2. Experimental

2.1. Chemicals

Citric acid (CA, ACS reagent, $\geq 99.5\%$), DL-malic acid (MA, ReagentPlus[®], $\geq 99\%$), phosphoric acid (ACS reagent, $\geq 85\%$ H₃PO₄) and ethylenediamine (ReagentPlus[®], $\geq 99\%$) were purchased from Sigma Aldrich. Quinine sulfate dihydrate (99+%, ACROS Organics[™]) was obtained from Fisher Scientific. The Biotech cellulose ester (CE) membrane (MWCO 100–500 D) was obtained from Spectrum Labs. Deionized water was produced by a Millipore Milli-Q system (Billerica, MA), and used through all experiments. All other reagents were of analytical grade and used without further purification. Difco[™] LB broth (Miller) and Difco[™] agar (granulated) were purchased from Becton, Dickinson, and Company. Dulbecco's phosphate-buffered saline (DPBS) was purchased from Mediatech, Inc. Sodium chloride (NaCl) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were purchased from Sigma Aldrich.

2.2. Synthesis of amorphous polymeric carbon dots

The synthesis was adopted from previous reports [8] with minor modifications. To synthesize the CACDs, a 4 M aqueous citric acid stock solution was prepared in advance. 2 mL of this stock solution was transferred into a 100-mL beaker, and then 540 μ L of ethylenediamine was added. The reaction was completed within 1 min as heat was released and a homogenous solution was formed. The mixture was stirred for 30 min and allowed to cool. Then, the colorless transparent mixture was transferred to a domestic microwave oven and heated under 360 W for 3 min. The resultant orange-yellow foamy solid was cooled in a fume hood for 20 min before 10 mL of MQ water was added into the beaker. The obtained reddish-brown transparent solution was dialyzed for 24 h to remove unreacted precursors. Then, rotary evaporation was used to remove most of the water in the solution, leaving behind a brown solid product at the bottom. Further drying was completed in an oven at 40 °C for one day.

To generate varied phosphorus-doped citric acid polymeric carbon dots (the CA-P-CD series), 2 mL of citric acid stock solution was poured into a beaker, and then 34 μ L of phosphoric acid was added. After mixing for 10 min, 540 μ L ethylenediamine was added. The subsequent procedure was the same as followed for the CACDs. Thus, CA-P-CDs-1 were obtained. To synthesize CA-P-CDs-2, 3 and 4, phosphoric acid was added in quantities of 68, 136 and 272 μ L, respectively. The final products of the CACDs and CA-P-CDs series were all yellow powders with gradually darker yellow color with increasing amount of doped phosphorus (Fig. S1A).

For the synthesis of MACDs and the MA-P-CD series (phosphorus-doped malic acid polymeric carbon dots), malic acid was

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